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UCRL-TR-202194-Rev-2

Lawrence Livermore National Laboratory (LLNL) Oxide Material Representation in the Material Identification and Surveillance (MIS) Program Revision 2

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June 29, 2004

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

MIS Working Group Concurrence

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Lawrence Livermore National Laboratory (LLNL)
Material Representation
In the Material Identification and Surveillance (MIS) Program

1. Introduction

The Materials Identification and Surveillance (MIS) program was established within the 94-1 R&D Program to confirm the suitability of plutonium-bearing materials for stabilization, packaging, and long-term storage under DOE-STD-3013-2000. Oxide materials from different sites were chemically and physically characterized. The adequacy of the stabilization process parameters of temperature and duration at temperature (950°C and 2 hours) for eliminating chemical reactivity and reducing the moisture content to less than 0.5 weight percent were validated. Studies also include surveillance monitoring to determine the behavior of the oxides and packaging materials under storage conditions. Materials selected for this program were assumed to be representative of the overall inventory for DOE sites. The Quality Assurance section of the DOE-STD-3013-2000 required that each site be responsible for assuring that oxides packaged according to this standard are represented by items in the MIS characterization program. The purpose of this document is to define the path for determining if an individual item is "represented" in the MIS Program and to show that oxides being packaged at Lawrence Livermore National Laboratory (LLNL) are considered represented in the MIS program. The methodology outlined in the MIS Representation Document (LA-14016-MS) for demonstrating representation requires concurrence of the MIS working Group (MIS-WG). The signature page on this document provides for the MIS-WG concurrence.

2. Criteria for Represented Material

Criteria for representation are given in the MIS Representation Document (LA-14016-MS) (MIS Doc.), entitled: *"Representation of Items Packaged to DOE-STD-3013-2000."* Materials are defined as represented if they meet the contained definition: "*A plutonium-bearing oxide material is represented by the MIS Program if the existing MIS inventory items can reasonably model and predict behavior of that material in long-term storage in a 3013 container."*

The MIS Doc. outlines three basic methods by which representation in MIS can be demonstrated by comparison to items in the MIS program. These methods are, in preferential order:

- Analytical Characterization
- Process History
- Prompt Gamma Comparison

Analytical Characterization

For oxides where trace impurities analysis is available, the relevant impurities present in an item can be compared to the relevant impurities present in the suite of materials in the MIS sample inventory. If no match is found, meaning that the impurities (or the impurity concentrations) present in the item are expected to influence the storage characteristics in a significantly different manner from the impurities in any existing MIS sample (a judgment to be made by the sites and verified by the MIS-WG), a new sample needs to be added to the MIS inventory that approximates this material composition.

Process History
Materials that are from processes that have actual samples in the MIS program are clearly represented. Much of the confidence in process history is due to process quality control at the time of production. Plutonium materials were produced to strict specifications ensured through quality control strategies including process flowsheets and testing via analytical chemistry methods. Sites can rely on MIS items from other sites if approved by the MIS-WG, who will verify that the processes employed at the different sites were known to generate similar product.

Prompt Gamma
If trace analysis is not available and the process history is not known, (a situation that will be encountered), the results of the item's prompt gamma measurements need to be compared with such measurements of MIS items. Items that show prompt gamma spectra with peaks that coincide with those of MIS samples are considered to be represented. Items with a prompt gamma spectrum that is significantly different from those of existing MIS samples will be evaluated by the MIS-WG to identify what actions need to be taken to ensure each item is represented. Since the material would already be packaged to DOE-STD-3013-2000, the complete container may be sent to the MIS program for sampling and repackaging.

3. LLNL Inventory Represented in MIS

The LLNL approach to demonstrating representation in MIS utilizes the Prompt Gamma comparison method.

The plutonium processing at LLNL has been mostly research and development (R&D). Therefore our materials are not identified into groups such as the IDCs or IDESs. For packaging of the LLNL materials, items were sorted into groups based on information about:

Form (metal, oxide, and salt)
Plutonium content (wt% Pu)
Plutonium Isotopic percentages (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu)
Uranium Content
^{241}Americium Content
^{237}Neptunium Content
Other specific information

Information from the draft MOX criteria was used in developing the groupings.

The majority of processes performed at LLNL are pyrochemical, foundry, or machining. The pyrochemical operations include direct oxide reduction (DOR), electrorefining (ER), calcining, molten salt extraction (MSE), salt scrub, metal casting, hydride followed by casting (HYDEC), and Hydride-Oxidation (HYDOX). Most of the pyrochemical operations were conducted with $CaCl_2$, KCl, NaCl, or $MgCl_2$ and calcium metal as a reductant. These operations are predominantly conducted in tantalum or magnesia crucibles and may produce residues that may be further processed to recover the actinides or to make safe for storage. LLNL does not do fluoride reduction (bomb reduction). Foundry and machining operations generate metal slag and turnings that are calcined to make safe for storage and may contain impurities that are typically found in weapons grade material or in processing equipment. LLNL also has a small aqueous line where materials are recovered by dissolution and oxalate or hydroxide precipitation. As part of the processing to meet the DOE-STD-3013, low purity oxides were washed to remove all water-soluble compounds, such as the chloride salts.

Prompt Gamma Comparison
When adequate analytical characterization, process knowledge or history is not available, the MIS representation document allows for representation to be determined by comparison of the prompt gamma spectrum of the item in question with the spectra of samples in the MIS program. It is recognized that this is the least desirable method to ensure representation. The prompt gamma spectra will be obtained after the oxides are packaged into 3013 cans.

For materials that have unique prompt gamma spectra, the MIS working group will review these items and make a recommendation. They may recommend shipment of completed 3013 items to the MIS inventory program, request the container be opened and sampled, or other means to demonstrate representation. The instance of a unique prompt gamma spectra is not expected to be a frequent occurrence.

Table 1 contains the results of prompt gamma spectrum analysis of the existing MIS inventory. This material is binned into a number of groups. Table 2 contains the grouping of the LLNL 3013 cans based on prompt gamma analysis and the representative MIS inventory items for each grouping. Table 2 also contains the LLNL 3013 can numbers with prompt gamma spectra analyzed so far and are cross referenced to items in the MIS inventory.

The material was grouped based on key elements that are expected to potentially present problems with corrosion, pressurization or other concerns. The first two compounds of interest are chlorides and fluorides. They are of concern because of their potential to corrode the containers. Any materials that did not contain elements of concern were placed into the other category.

4. Documentation

Each 3013 container of oxide processed has an associated data file that includes feed item identification. The 3013 data file will indicate whether:

1. The material is represented by prompt gamma spectra similarity, or
2. The item has a dissimilar prompt gamma spectra and MIS has recommended representation by other means based on MIS-WG evaluation.

5. Conclusion

Representation of LLNL generated 3013 oxide cans will be demonstrated based on prompt gamma spectra comparison using provisions described in the representation definition document. The MIS may request additional samples, or more likely complete items, of unusual or unique items discovered during performance of this activity.

Therefore, there is a path forward for the use of gamma spectra comparison, thus providing assurance that all items are represented in the MIS inventory program.

Table 1: Table of Prompt Gamma Data from MIS Inventory Items

Group	MIS Cat	MIS Item Name	Al	Be	Cl	Cr	Cu	F	Mg	K	Na	Si	Ta
Chloride	1A Chloride	101707001A			Cl						Na		
		ARF-102-85-223			Cl				Mg	K	Na		
		C00695			Cl				Mg	K	Na		
		CLLANL025			Cl				Mg	K	Na		
		PMA-XBS			Cl					K	Na		
		C00024A		Be	Cl				Mg		Na		
	1B Chloride with Fluoride	07032282A			Cl			F	Mg		Na		
		ARF-102-85-295			Cl			F	Mg	K	Na		
		ARF-102-85-355			Cl			F	Mg		Na		
		ARF-102-85-365			Cl			F	Mg	K	Na		
		MISNE4	Al		Cl			F	Mg	K	Na	Si	
		053038	Al	Be	Cl			F	Mg		Na		
Fluoride	2A Strong Fluoride	07161856		Be				F			Na		
		07242201A	Al					F	Mg		Na	Si	
		YBG2-NRDL-4						F					
	2B Weak Fluoride	07242165A	Al					F	Mg		Na	Si	
		07242243A						F					
		07242326A											
		PuUOXBC05						F	Mg		Na		
High Mg	3 Items containing $Mg(OH)_2$	H10-R437	Al						Mg		Na	Si	
		H10-R438							Mg		Na	Si	
		H10-R439	Al						Mg		Na		
		H11-R440							Mg				
		H11-R441							Mg				
		H11-R442							Mg				
		H11-R443							Mg				
Other Impurities	5A Other Prompt Gamma Impurities	5501407		Be							Na		
		669194		Be							Na		
		ARF-102-85-114-1		Be							Na		Ta
		CAN92		Be									
		BLO-39-11-14-004									Na		Ta
		HUD6-PSU-84-06-05									Na		
		MISNE2									Na		
		PBO-47-09-012-023									Na		
		PPSL-365									Na		
		SCP711-46									Na		
	5B No Prompt Gamma Impurities	5501579											
		PEOF1											
		SCP711-56											
Not Binned	Not Binned	07242141A						F			Na		
		MT-1490									Na		

Table 2: Table of LLNL 3013 Oxides

Group	PG Representation	3013 Container ID	Al	Be	Cl	Cr	F	Mg	K	Na	Comments
Chloride	1A. Chloride	L000076			Cl					Na	
		L000155	Al		Cl			Mg		Na	
		L000167			Cl			Mg		Na	
		L000181			Cl			Mg		Na	
	1C. Chloride Containing Be	L000214		Be	Cl			Mg		Na	
	1D. Chloride Containing Be & F	L000204		Be	Cl		F	Mg		Na	Strong Mg
		L000217		Be	Cl		F	Mg		Na	Strong F, Mg
		L000223	Al	Be	Cl		F	Mg		Na	Strong Al, F, Mg
Fluoride	2A. Strong Fluoride	L000158	Al	Be			F	Mg		Na	
		L000177					F	Mg		Na	
		L000179	Al	Be			F	Mg		Na	Strong Al, Mg
		L000182	Al	Be			F	Mg		Na	Strong Al
		L000186	Al	Be			F	Mg		Na	Strong Al
		L000220	Al				F	Mg		Na	Strong Mg
		L000227		Be			F	Mg		Na	Strong Mg
	2B. Weak Fluoride	L000157	Al	Be			F	Mg		Na	Strong Al
		L000169					F				
		L000178	Al	Be			F	Mg		Na	Strong Al
		L000180	Al	Be			F	Mg		Na	Strong Al
		L000184	Al	Be			F	Mg		Na	Strong Al
		L000185	Al				F	Mg		Na	Strong Al, Mg
		L000228	Al	Be			F	Mg		Na	Strong Al, Mg
Other Impurities	4. Items Containing Be	L000058		Be							
		L000075		Be							
		L000152		Be				Mg		Na	Strong Mg
		L000153	Al	Be						Na	
		L000156		Be						Na	
		L000159	Al	Be				Mg		Na	Strong Al
		L000162	Al	Be						Na	
		L000164	Al	Be						Na	
		L000165		Be						Na	
		L000172	Al	Be						Na	
		L000174	Al	Be							Strong Al
		L000175	Al	Be				Mg		Na	Strong Al
		L000176		Be						Na	
		L000191	Al	Be				Mg		Na	Strong Al
		L000194		Be						Na	
		L000195		Be				Mg		Na	
		L000196	Al	Be				Mg		Na	
		L000199	Al	Be				Mg		Na	Strong Al
		L000202	Al	Be				Mg		Na	
		L000203	Al	Be				Mg		Na	
		L000206		Be				Mg		Na	

Table 2: Table of LLNL 3013 Oxides (Continued)

Group	PG Representation	LLNL 3013 Container ID	Al	Be	Cl	Cr	F	Mg	K	Na	Comments
Other Impurities (Continued)	4. Items Containing Be (Continued)	L000207	Al	Be				Mg		Na	
		L000209		Be				Mg		Na	
		L000211		Be				Mg		Na	
		L000219		Be				Mg		Na	Strong Mg
		L000221		Be				Mg		Na	Strong Mg
		L000224	Al	Be				Mg		Na	
		L000225		Be						Na	
		L000226		Be				Mg		Na	
	5A. Trace Impurities Al Mg Na	L000071								Na	
		L000072								Na	
		L000073						Mg			
		L000074								Na	
		L000077								Na	
		L000151								Na	
		L000163								Na	
		L000166								Na	
		L000170								Na	
		L000171						Mg		Na	
		L000173	Al					Mg		Na	Strong Al
		L000205	Al					Mg		Na	Strong Al, Mg
		L000212								Na	
	5B. No Impurities by Prompt Gamma	L000062									
		L000063									
		L000154									
		L000193									